Color Characteristics and Stability of Nonbleeding Cocktail Cherries Dyed with Carotenoid Pigments

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ABSTRACT

Experimental cocktail cherries dyed with carotenoids and commercial cherries were compared by spectrocolorimetry to determine color characteristics and stability. Cherries dyed with canthaxanthin, apo-carotenal and oleoresin paprika were more tomato- or orange-red than cherries dyed with Red No. 40, Red No. 3, or carmine. No color bleeding was observed with carotenoid-dyed cherries. The color of cherries dyed with canthaxanthin was stable for 1 year at 4°C. Color stability was not as good in cherries dyed with apo-carotenal but could be improved greatly by addition of ethylenediaminetetraacetic acid (EDTA) and ascorbic acid to preservative solutions in which cherries were stored.

Key Words: cherries, color, carotenoids, apo-carotenal, canthaxanthin

INTRODUCTION

CHERRIES for fruit cocktail and fruit salad are artificially colored with a red dye that is "fixed" within the cherry tissue so that the dye cannot "bleed" into the syrup or other fruit ingredients to give them a pink hue. For many years, cocktail cherries were colored with FD&C Red No. 3 (erythrosine), a xanthine dye, by infiltrating an alkaline solution of this colorant into the desulfited fruit and then precipitating the dye by soaking the fruit in an acidic solution (Waters and Woodroof, 1986). In 1990, the use of this colorant in cherries became inadvisable as a result of action by the U.S. Food & Drug Administration (FDA) to remove Red No. 3 from approval for cosmetic uses because it caused thyroid tumors in rats (Anon., 1990). Future action to ban the use of Red No. 3 in cocktail cherries was expected (Borzelleca and Hallagan, 1992).

As an alternative to Red No. 3, some producers of cocktail cherries have switched to carmine, the aluminum or calcium-aluminum lake of carminic acid (water-insoluble complex on aluminum hydroxide substrate), solubilized with a dilute alkali solution. This also can be "fixed" within the fruit tissue by some proprietary processes. Carmine is derived from cochineal, the dried body of an insect, *Dactylopius coccus costa (Cossus cacti* L.) found in the Canary Islands and Peru (Anon., 1981). This colorant lacks Kosher certification and is reputed to be of high cost and difficult to apply (Duxbury, 1990).

Recognizing the need for other means of producing nonbleeding cocktail cherries, we developed and patented a process for dyeing cherries with red-colored carotenoids which are water-insoluble but can be infiltrated into the cherry flesh in ethanol (Sapers, 1991). The color of cherries produced by this process was similar to that of commercial cherries, and in preliminary studies, appeared to be stable during storage. The objectives of our research were to compare the color characteristics of cherries, dyed with carotenoids according to the USDA process or with alternative commercial colorants, and to determine the color stability of cherries dyed with carotenoids by quantitative measurement of reflectance parameters.

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MATERIALS & METHODS

Preparation of cocktail cherries

Experimental cherries were prepared by the USDA patented procedure (Sapers, 1991), modified as described below. Carotenoid solutions to be used for dyeing desulfited, brined cherries were prepared by dissolving 0.03% β-apo-8'-carotenal (synthetic, prepared from Roche 20% apo-carotenal suspension in vegetable oil; Roche Vitamins and Fine Chemicals, Nutley, NJ), 0.2% canthaxanthin (synthetic, prepared from Roche Dry Canthaxanthin 10% SD, a spray dried dispersion of canthaxanthin in gelatin, sucrose and vegetable oil), or 0.5% oleoresin paprika (Meer H-2500; Meer Corp., North Bergen, NJ) in anhydrous ethanol (U.S.P.). These colorants are all approved food additives, exempt from certification. The canthaxanthin solution was prepared by dispersing 20g dry colorant powder in 600 mL ethanol with a Polytron PCU-2 Homogenizer (Brinkmann Instruments Co., Westbury, NY), operated at high speed for 5 min, and then heating the suspension to boiling on a steambath. The suspension was cooled and filtered through Whatman No. 541 filter paper under vacuum. Residual canthaxanthin in the filter cake was extracted with four successive 100 mL portions of boiling ethanol. All canthaxanthin extracts were filtered, as described, and combined. (This modification of the patented procedure eliminated the need to use chloroform and methanol in the preparation of canthaxanthin solutions).

Brined cherries, from a commercial maraschino processor, were leached in cold running water for 25 hr to reduce sulfur dioxide content to about 100 ppm, estimated by titrating a diluted, homogenized fruit sample with 0.02N I_2 with a 1% starch indicator. Leached cherries (1200g) were then soaked in two successive 2400 mL portions of ethanol to displace sufficient tissue water so that ethanol in equilibrium with cherries after the second soak was 96%, measured with an alcohol hydrometer. Ethanolic cherries were drained and added to carotenoid solutions using a ratio of solution to cherries of about 2:1 for apo-carotenal and oleoresin paprika and 1:1 for canthaxanthin. Cherries were equilibrated in carotenoid solutions at ambient temperature (≈20°C) for 16 hr with apo-carotenal, 3 hr with canthaxanthin, and 5-days with oleoresin paprika. After dyeing, the cherries were rehydrated in running water to displace the ethanol and precipitate infiltrated carotenoids within the cherry tissue. Rehydration was continued until the alcohol concentration for water in equilibrium with the cherries (measured with an alcohol hydrometer) was reduced to 4%. After rehydration, dyed cherries were packed in a sugar syrup or preservative solution.

Evaluation of cherry color characteristics

Experimental cherries dyed with carotenoids were compared with commercially prepared maraschino cherries containing FD&C Red No. 40 as colorant and with non-bleeding cocktail cherries, dyed with FD&C Red No. 3 or carmine, that had been removed from commercially canned fruit cocktail. To determine whether cherries dyed with carotenoids were subject to bleeding, cherry pieces were removed from opened cans of fruit cocktail and replaced with experimental cherries, cut into quarters. Portions of fruit cocktail containing commercial or experimental cherries were heated in beakers to 95°C in 25 min and then cooled to 40°C in 60 min. The syrup and fruit pieces in each fruit cocktail sample were observed for any color changes indicative of bleeding.

Cherry surface color was evaluated by reflectance measurements made with a spectrocolorimeter (The Color Machine, Byk Gardner, Silver Spring, MD), using illuminant C (representing average daylight), 10° observer, and an averaging mode with four replications per sample. The instrument was calibrated externally with a standard white tile. Cherries were blotted on paper toweling to remove excess syrup or preservative solution and then placed over a 10 mm aperture at the

Table 1—Composition of syrup and preservative solutions for evaluation of cherry color stability during storage

Solution	Acetic acid[a]	Sodium benzoate	Percent (w/v) Citric acid	Ascorbic acid	EDTA[b]	$CaCl_2$	Sucrose
1	3	0.4	–	–	–	–	–
2	3	0.4	0.1	–	–	–	–
3	3	0.4	–	0.05	–	–	–
4	3	0.4	–	–	0.03	–	–
5	3	0.4	0.1	0.05	–	–	–
6	3	0.4	–	0.05	0.03	–	–
7	3	0.4	–	–	–	0.2	–
8	–	0.4	1	–	–	–	–
9	–	0.4	1	0.05	–	–	–
10	–	0.4	0.3	–	–	–	10

[a] Added as distilled white vinegar, 5% acidity.
[b] Calcium disodium EDTA, Food Grade.

sample port so that the tristimulus coordinates L*, a*, and b* (CIELab color scale) and reflectance spectra could be obtained. Values of L* indicate lightness or darkness (higher values are lighter). Values of hue angle ($\tan^{-1}$ b*/a*), indicate sample color (0° = red-purple, 90° = yellow, 180° = bluish green, 270° = blue), and chroma [$(a^{*2} + b^{*2})^{1/2}$], indicate color purity (high values are more vivid), were calculated from the tristimulus coordinates a* and b* (McGuire, 1992).

In addition, visible absorption spectra were obtained for ethanol solutions of the carotenoid colorants and for aqueous solutions of FD&C Red No. 3 (in 0.05% $NaHCO_3$) (Crompton & Knowles Corp., Mahwah, NJ), FD&C Red No. 40 (Crompton & Knowles Corp.), and water soluble carmine (Crompton & Knowles Corp.) with a diode array UV-visible spectrophotometer (Model 8452A, Hewlett-Packard, Palo Alto, CA).

Storage studies

The color stability of cherries dyed with apo-carotenal or canthaxanthin was investigated in samples packed in 10° Brix syrup, or in preservative solutions that might be used during storage of dyed cherries prior to packing in fruit cocktail. Preservative solutions included various combinations of acetic acid (distilled white vinegar, 5% acidity), sodium benzoate, citric acid, ascorbic acid, the calcium disodium salt of ethylenediaminetetraacetic acid (EDTA), and calcium chloride (Table 1). A constant ratio of cherries-to-syrup (or preservative solution) and fill of container were used to ensure uniform treatment and exposure to O_2 during storage. Samples were stored in the dark at ambient temperature (≈20°C) for 1 yr. Cherry color was measured with the spectrocolorimeter at 3-wk intervals. To determine the effects of iron contamination on cherry color stability, one set of apo-carotenal-dyed samples was desulfited and then rehydrated after dyeing in metal containers showing visible rust. All other samples were prepared in glass containers with no exposure to metal.

RESULTS & DISCUSSION

Bleeding of cherries dyed with carotenoids

An essential requirement of colorants for cocktail cherries is the absence of color bleeding during processing and storage of fruit cocktail. The syrup and fruit components of fruit cocktail samples containing commercial cherries or experimental cherries dyed with carotenoids showed no evidence of bleeding after the fruit cocktail had been heated and cooled. The finding that bleeding did not occur with carotenoid-dyed cherries was consistent with the reported insolubility of these carotenoids in water (Gordon, 1977). Carotenoid insolubility also accounts for the very faint color seen in water used to rehydrate the freshly dyed cherries. Carotenoid precipitation within the cherry tissue must occur during the initial penetration of water into the ethanolic fruit since both canthaxanthin and apo-carotenal are only slightly soluble in ethanol as well as being insoluble in water.

Color characteristics of cherries dyed with carotenoids

Comparison of experimental cocktail cherries (dyed with carotenoids) with commercial maraschino and cocktail cherries by tristimulus colorimetry revealed important differences in reflectance parameters (Table 2). The color of cocktail cherries, dyed with Red No. 3, was lighter (higher L*), more vivid (higher chroma), and less yellow-red (lower hue angle) than maraschino cherries, dyed with Red No. 40. Reflectance spectra for the cocktail cherries showed higher spectral percent values at 460 nm, indicative of a bluer color (Billmeyer and Saltzman, 1981). Cocktail cherries, dyed with carmine, were more like Red No. 40 than Red No. 3 in chroma and hue angle values. Reflectance spectra for carmine-dyed cherries were similar to those for cherries dyed with Red No. 3 at 460 nm but showed higher spectral percent values at 540 nm, in the green region of the visible spectrum. Spectral percent values for all commercial cherries were similar at 640 nm, in the red region.

Experimental cherries dyed with canthaxanthin and apo-carotenal had higher chroma and hue angle values than commercial maraschino and cocktail cherries, indicative of a more yellow-red color than that of the commercial cherries. Cherries dyed with oleoresin paprika were also yellow-red (based on hue angle value), but darker (lower L*), less vivid (lower chroma value), and less intensely red (lower spectral percent value at 640 nm) than cherries dyed with the other carotenoids. Visually, the experimental cherries appeared more orange or tomato red, compared to the bluer hue of the commercial cherries.

These observations were consistent with the color and visible absorption maxima of the colorants in solution (Table 3). The more orange-red carotenoid solutions had absorption maxima at lower wavelengths than the other colorant solutions. Davies (1976) reported visible absorption maxima for apo-carotenal, canthaxanthin, and capsanthin in ethanol at 463, 474, and 476 nm, respectively.

Color stability of cherries dyed with carotenoids

Apo-carotenal. The color of carotenoid-dyed cocktail cherries must be stable during storage, both prior to packing in fruit cocktail and after the final product has been processed and is in the distribution system. In initial storage studies, cherries that were dyed with apo-carotenal and packed in a vinegar-benzoate preservative solution (Soln. 1, Table 1), showed fading, indicated by an increase in L*, and a change in color from red to orange or yellow, indicated by an increase in the hue angle and decrease in reflectance at 640 nm (Fig. 1). These changes were greater and occurred more rapidly in samples prepared in metal containers where iron contamination was likely than in samples prepared in all-glass containers, although by 15 weeks, these samples were similar. Addition of EDTA (Soln. 4) and ascorbic acid (Soln. 3) to preservative solutions diminished but did not eliminate the destabilizing effect of metal exposure, as indicated by the large change in hue angle and reflectance at 640 nm during storage. The substantial change in color of cherries prepared in glass during 15 wk of storage at 20°C, demonstrated a need to add antioxidants and/or chelating agents to improve color stability.

A second storage study with apo-carotenal-dyed cherries confirmed the low stability of this colorant in samples packed in the vinegar-benzoate preservative solution (Soln. 1) or in syrup (Soln. 10) (Fig. 2). Small increases in L*, indicative of fading, and larger increases in the hue angle and decreases in the spectral percent value at 640 nm occurred gradually over 51 weeks at 20°C. These changes were consistent with the observed color change from tomato-red to orange, or in the extreme case, yellow. The presence of residual ethanol in the preservative solution, as might result from incomplete rehydration of cherries after dyeing, accelerated this process. The color could be stabilized for at least one year at 20°C by adding both ascorbic acid and EDTA to the preservative solution (Soln. 6). These compounds, used individually, were only partially effective in protecting cherry color (data not shown). Substi-

Table 2—Color characteristics of commercial and experimental cherries

Cherry	Colorant	Tristimulus parameter			Reflectance, spectral percent			
		L*	Chroma[a]	Hue Angle (°)[b]	460 nm	500 nm	540 nm	640 nm
Commercial								
Maraschino	Red No. 40	31.0±2.1	31.0	25.9	3.68	3.40	3.57	22.25
Cocktail A	Red No. 3	36.6±0.7	36.1	14.4	6.66	3.99	3.13	25.14
Cocktail B	Carmine	33.7±2.3	28.2	24.8	4.89	4.19	4.83	20.20
Cocktail C	Carmine	39.1±2.5	29.4	22.8	7.20	5.97	6.74	25.98
Experimental								
Cocktail	Canthaxanthin	35.0±1.8	45.4	42.1	2.33	2.27	2.95	27.02
Cocktail	Apo-carotenal	37.5±1.1	40.6	40.2	3.57	3.58	4.52	29.36
Cocktail	Oleoresin paprika	29.3±2.5	27.5	36.6	2.92	2.79	3.02	14.99

[a] $(a^{*2} + b^{*2})^{1/2}$.
[b] $\text{Tan}^{-1}\ b^*/a^*$.

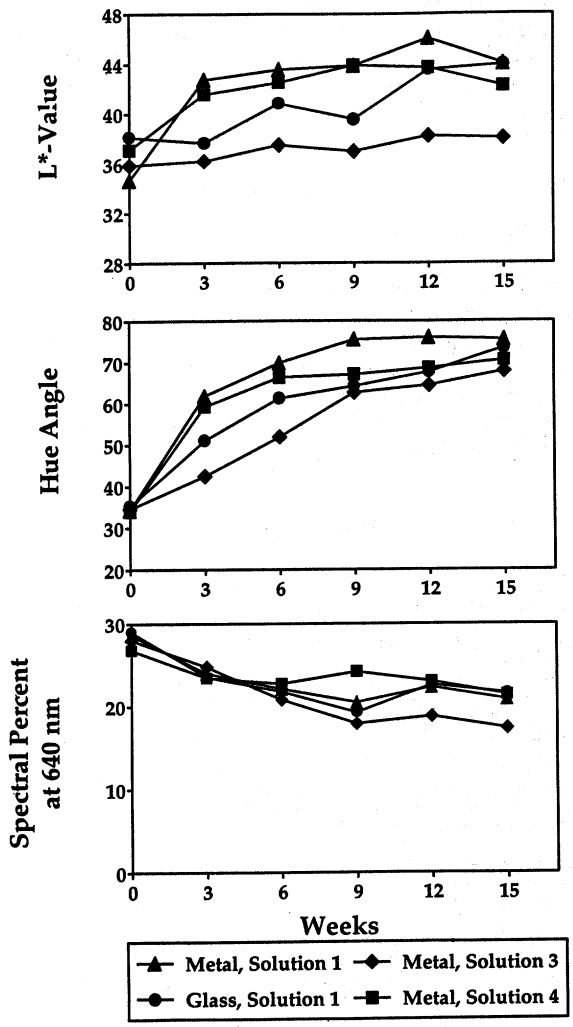

Fig. 1—Color stability of cocktail cherries, processed in metal or glass containers, dyed with apo-carotenal, and stored at 20°C in dark in: (see Table 1) Solution 1, vinegar + benzoate; 3, vinegar + benzoate + ascorbic acid; 4, vinegar + benzoate + EDTA.

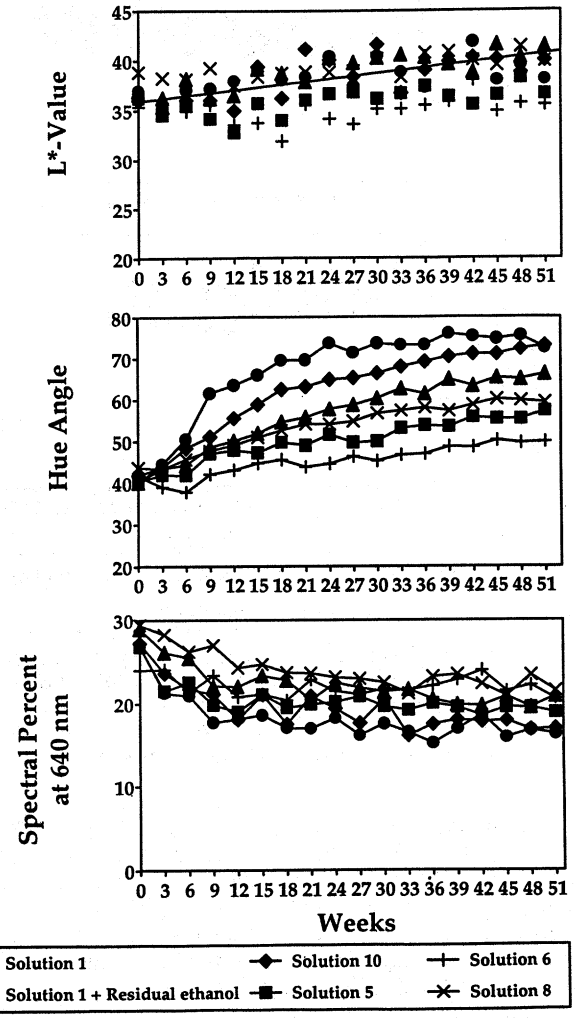

Fig. 2—Color stability of cocktail cherries, dyed with apo-carotenal, and stored at 20°C in dark in: (see Table 1) Solution 1, vinegar + benzoate; 1 + residual ethanol; 5, vinegar + benzoate + citric acid + ascorbic acid; 6, vinegar + benzoate + ascorbic acid + EDTA; 8, citric acid + benzoate; 10, syrup (sucrose + citric acid + benzoate).

Table 3—Visible absorption maxima and color of cherry colorant solutions

Colorant	Solvent	λ_{max} (nm)	Color
Red No. 40	Water	504	Orange-red
Red No. 3	0.05% $NaHCO_3$	526	Pink-red
Carmine (water soluble)	Water	516, 552	Violet-red
Canthaxanthin	Ethanol	466	Tomato-red
Apo-carotenal	Ethanol	488	Orange-red
Oleoresin paprika	Ethanol	454, 474	Orange-red

tution of citric acid for vinegar in the preservative solution (Soln. 8) and addition of citric acid with ascorbic acid to the preservative solution (Soln. 5) also provided partial protection to cherry color during storage. The change in hue angle was 30–50% less than that of cherries packed in vinegar benzoate or syrup. During storage, cherry samples packed in preservative solutions containing ascorbic acid alone (Soln 3, Table 1) or ascorbic acid in combination with citric acid (Soln 5), but not ascorbic acid in combination with EDTA (Soln 6), were more fragile than other samples. The cause of this defect, which appeared to involve a weakening of the cherry skin, is not known.

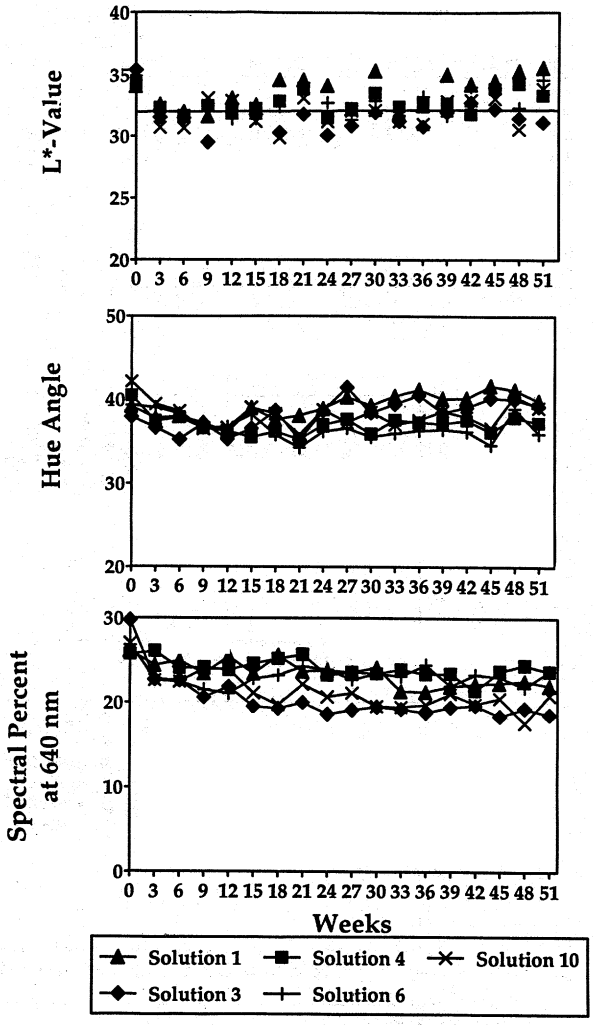

Fig. 3—Color stability of cocktail cherries, dyed with canthaxanthin, and stored at 20°C in dark in: (see Table 1) Solution 1, vinegar + benzoate; 3, vinegar + benzoate + ascorbic acid; 4, vinegar + benzoate + EDTA; 6, vinegar + benzoate + ascorbic acid + EDTA; 10, syrup (sucrose + citric acid + benzoate).

Canthaxanthin. Changes in L*, hue angle and reflectance at 640 nm for cherries dyed with canthaxanthin and then stored in syrup or preservative solutions were relatively small, indicating a high degree of color stability (Fig. 3). All samples showed an initial decrease in tristimulus parameters during the first 3 wk of storage. This probably reflected the replacement of water in the freshly prepared cherries with syrup or preservative solution rather than any color degradation. Thereafter, the cherries showed little or no change in L*-value, hue angle or reflectance at 640 nm during storage for one year. The high degree of stability of canthaxanthin in cherries was consistent with its demonstrated stability in several food products (Bunnel and Borenstein, 1967).

During storage, cherries packed in vinegar-benzoate with added ascorbic acid (Soln. 3) visually appeared to darken, although no parallel change in tristimulus or spectral data was seen. Such darkening may be an indication of the nonenzymatic browning of dehydroascorbic acid, generated by the oxidation of added ascorbic acid during storage. The problem might be avoided by reducing the headspace volume or vacuum packing cocktail cherries. As with apo-carotenal, canthaxanthin-dyed cherries, packed in preservative solutions containing ascorbic acid, became more fragile during storage.

The improvements in color stability of cherries dyed with apo-carotenal and canthaxanthin, obtained by EDTA addition, implied that the color of carotenoid-dyed cherries may be destabilized by the presence of trace metals such as iron or copper. Metal contamination may occur during cherry processing prior to desulfiting and dyeing (Butland, 1952; Kitson and Strachan, 1955). Heavy metals such as iron may catalyze the oxidation of lipid components of the carotenoid colorants (Apo-carotenal and canthaxanthin products are both formulated with vegetable oils), generating hydroperoxides that oxidize the carotenoid colorants (Ingold, 1962; Davies, 1976).

Oleoresin Paprika. Controlled storage studies were not carried out with cherries dyed with oleoresin paprika. However, extensive fading was observed in a sample prepared for color evaluation after several months of storage at 4°C, presumably due to oxidation of the carotenoids. Because excellent color stability had been obtained with canthaxanthin, no further storage experiments were conducted with oleoresin paprika-dyed cherries.

CONCLUSIONS

THE COLOR of cocktail cherries, dyed with the carotenoid canthaxanthin, as an alternative to Red No. 3 or carmine, was nonbleeding, stable during storage, and comparable to the other colorants in color intensity, although more tomato-red in hue. The color of cherries dyed with apo-carotenal was similar to that of cherries dyed with canthaxanthin but less stable, especially in the presence of metal ions. Color stability can be greatly increased by addition of EDTA to the solution in which cherries are packed.

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Mention of brand or firm names does not constitute endorsement by the U.S. Dept. of Agriculture over others of a similar nature not mentioned.